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OBSERVATIONS ON PERMEATION
OF POLYTETRAFLUOROETHYLENE
BY COMPOUNDS OF RHENIUM,
MOLYBDENUM, AND TUNGSTEN

by Harold Leibecki

*Lewis Research Center
Cleveland, Ohio*

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ABSTRACT

Observations of diffusion of rhenium, molybdenum, and tungsten hexafluorides into polytetrafluoroethylene and hydrolysis of the resultant material are reported. Exposure of polytetrafluoroethylene to rhenium or molybdenum hexafluoride, followed by hydrolysis, results in impregnation of the plastic with a metal compound. Tungsten hexafluoride was observed to grow a fibrous product (composition unresolved) on the surface of the plastic during ambient air hydrolysis. Rhenium hexafluoride hydrolysis yielded a mixture of rhenium oxides. The polytetrafluoroethylene sample was investigated for electrical conduction and was found to be substantially more conductive than the pure plastic. The hydrolysis product of molybdenum hexafluoride impregnation was postulated to be a mixture of molybdenum oxides. The electrical conduction properties of the product were not investigated.

OBSERVATIONS ON PERMEATION OF POLYTETRAFLUOROETHYLENE BY COMPOUNDS OF RHENIUM, MOLYBDENUM, AND TUNGSTEN

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SUMMARY

It was observed that the hexafluorides of rhenium, molybdenum, and tungsten, when placed in contact with bulk polyfluorinated plastics, penetrate the polymer. It was further observed that the fluorides of rhenium and molybdenum can be hydrolyzed in situ to form metal compounds in the plastic. Thus, a process was discovered for impregnating polytetrafluoroethylene in the finished form with rhenium or molybdenum compounds.

The resulting product of rhenium impregnation and hydrolysis was a mixture of rhenium oxides (ReO_2 and Re_2O_3). The oxide-impregnated polytetrafluoroethylene had an electrical resistance many orders of magnitude less than the pure plastic. The specific resistance of the impregnated portion of a 1-centimeter cube of tetrafluoroethylene impregnated 1.2 millimeters deep with rhenium oxide was found to be 173 ohm-centimeters. Polytetrafluoroethylene and Re_2O - Re_2O_3 have specific resistances of 10^{18} ohm-centimeters and 1×10^{-4} to 3×10^{-4} ohm-centimeter, respectively. Hydrolysis of molybdenum hexafluoride impregnation produced a material that was postulated to be a mixture of molybdenum oxides. The electrical resistance of this process was not investigated.

Tungsten hexafluoride impregnated into polytetrafluoroethylene reacted differently from rhenium and molybdenum hexafluorides. The hydrolysis product of the polytetrafluoroethylene impregnation was observed to grow as fibers on the surface of the plastic. The composition and properties are as yet undetermined.

INTRODUCTION

During an investigation of inorganic compounds as solvents (ref. 1), it was observed that when rhenium hexafluoride was placed in contact with polytetrafluoroethylene (TFE) it penetrated the polymer and subsequently underwent an apparent chemical change on exposure to air. This phenomenon led to an investigation of the interaction of the hexafluorides of rhenium, molybdenum, and tungsten with TFE.

EXPERIMENTAL

Materials

Cubes machined from bulk TFE were used for impregnation studies. The cubes measured 1.00 ± 0.01 centimeter on an edge and had a density of 2.133 ± 0.001 grams per cubic centimeter.

Commercially available rhenium hexafluoride of 99-percent purity was used. The fluorine content of the material was found to be 38.48 percent compared with a theoretical content of 37.95 percent. Infrared analysis revealed a trace of hydrogen fluoride and an unknown having an absorbance at 625 reciprocal centimeters, as impurities. No oxy-fluoride compounds were observed in the spectrum and free fluorine, with a vapor pressure 760 millimeters at -188°C (85 K), would not be expected to be a contaminant.

Commercially available molybdenum hexafluoride of 99-percent purity and tungsten hexafluoride of 99.8-percent purity were used without further characterization.

Apparatus

Figure 1 is a diagram of the apparatus used for the impregnation of the TFE cubes. The diffusion chamber and the liquid reservoir were constructed from chlorotrifluoroethylene, the remainder were constructed of a nickel based alloy. The dip tube allows withdrawal of the liquid from the diffusion chamber. The diffusion chamber was coated on the inner surface with an epoxy resin base coating to prevent the impregnation of chlorotrifluoroethylene by the liquid. The assembled unit is shown in figure 2.

Procedure

The impregnation of TFE samples was accomplished in two steps. First, the sample was exposed to and impregnated with the metal fluoride. Second, the metal fluoride was hydrolyzed.

Impregnation. - The sample was placed in the diffusion chamber which was then evacuated through valve 1 (fig. 1). The impregnating liquid was introduced into the diffusion chamber by opening valve 2 (fig. 1), which allowed the liquid to be drawn up through the dip tube extending into the liquid reservoir. After the sample had contacted the metal fluoride, for a predetermined time, a positive pressure was applied to the diffusion chamber through valve 1. Valve 2 was then opened forcing the excess liquid back to the reservoir. When expulsion was complete, valve 2 was closed and valve 1 was

opened allowing the diffusion chamber to vent to the atmosphere, after which the diffusion chamber was disassembled and the sample was removed for hydrolysis.

Hydrolysis. - The metal fluoride impregnated sample can be hydrolyzed by reacting the sample in ambient air or immersing it in distilled water. No attempt was made to optimize the hydrolysis step. The conditions of hydrolysis in air or water were ambient temperature and pressure for 48 hours.

Instrumentation and Measurements

After hydrolysis of the hexafluoride impregnated samples they were coated on opposite faces with vapor-deposited gold. The gold coating served as electrical contacts for alternating- and direct-current (ac and dc) electrical resistance measurements. These measurements were made at $24 \pm 2^\circ \text{C}$ ($297 \pm 2 \text{ K}$).

Alternating-current measurements. - Alternating current (ac) resistance measurements were made using a transformer ratio-arm bridge over a frequency range of 20 to 20 000 hertz. The bridge had an accuracy of 0.1 percent. The applied voltage across the sample was 60 millivolts.

Direct-current measurement. - Direct-current measurements (dc) were obtained by applying a constant voltage of from 0 to 1 volt across the sample and measuring the resulting current. The voltage across the sample was measured with a differential voltmeter having a 100-megohm input impedance and an accuracy of 0.05 percent. The current was measured with an electrometer having an accuracy of 3 percent of full scale from 10^0 to 10^{-10} ampere.

RESULTS AND DISCUSSION

Rhenium Impregnation

Metallographic studies showed that the depth of rhenium penetration is dependent on the length of time the sample is in contact with rhenium hexafluoride. Figures 3 and 4 are cross sections of TFE cubes after 24 and 72 hours of diffusion time in rhenium hexafluoride. The penetration of rhenium was found to be 0.8 and 1.2 millimeters, respectively.

The X-ray diffraction data in table I was identified as representative of a mixture of the rhenium oxides, ReO_2 and Re_2O_3 (unpublished data from Chase Brass & Copper Company, Cleveland, Ohio). This pattern was obtained by electron and X-ray diffraction studies of the impregnated material after eliminating diffraction data due to TFE.

Electronphotomicrographs revealed that the rhenium oxide particles are small, with a tendency to agglomerate. This characteristic is shown in figure 5. The texture shown in the figure is due to blade chatter during microtoming of the sample. The texture is more clearly shown in figure 6, which is a microtomed section of the unimpregnated TFE.

The presence of rhenium oxide in cube 2 (fig. 4) decreased its electrical resistance by 16 orders of magnitude.

The resistance of pure mixed $\text{ReO}_2 - \text{Re}_2\text{O}_3$ is 1×10^{-4} to 3×10^{-4} ohm-centimeter (unpublished data from Chase Brass & Copper Company, Cleveland, Ohio), while that of bulk TFE is greater than 10^{18} ohm-centimeters (see table II).

A portion of the resistance of cube 1 (fig. 3) is believed to be due to poor electrical contacts. This is shown by the change in specific resistance in cube 2 when different methods of vapor depositing the contacts are used. The vapor deposition procedure used in method B differs from method A by the back sputtering cleaning step prior to vapor deposition of the gold.

It is apparent that a difference exists between the ac and dc resistance values. The existence of semiconductor properties of the impregnated cubes were investigated by switching the polarity of the dc voltage. The presence of a barrier layer or a p-n junction would cause a change in resistance with a change in polarity. Because this did not occur, general semiconductor theory cannot explain the observed difference between ac and dc resistance values.

Table III shows the dependence of conduction and capacitance on frequency from 20 000 to 50 hertz.

There is a slight decrease in conductivity over the frequency range of 20 000 to 1000 hertz. From 1000 to 50 hertz, the conductivity is essentially constant. Capacitance follows an inverse conduction-frequency relation. From 20 000 to 1000 hertz the capacitance is constant, and from 1000 to 50 hertz the capacitance increases. This phenomenon cannot be correlated to known electrical circuitry, and therefore no reason can be given for the differences in the ac and dc resistance values.

Molybdenum Impregnation

The occlusion of the hydrolysis product of molybdenum hexafluoride in TFE is shown in figure 7. The resolution is not as good as in the case of rhenium (figs. 3 and 4) because the color contrast is poor.

The impregnated material was a light green color which slowly turned blue. Molybdenum possesses a variety of oxide compositions between MoO_2 and MoO_3 many of which are highly colored. Therefore a change of oxidation state and color would not be uncommon. This phenomena of color variation has been observed by Ames and Gregor

(ref. 2). The color of molybdenum oxide they produced varied from deep blue to blue-green, which was reported as being due to small amounts of molybdenum oxides of lower oxidation states than MoO_3 .

X-ray diffraction patterns for the compound were not identifiable. However, spectrographic analysis showed that molybdenum was present in the impregnated material. From the spectrographic analysis and the color phenomenon observed and reported by Ames and Gregor, it is believed that the material was a mixture of molybdenum oxides. The electrical conduction of this material was not investigated.

Tungsten Impregnation

Tungsten hexafluoride also penetrated TFE, but rather than resulting in discrete particles within the TFE on hydrolysis in air, fibers were formed on the surface, as shown in figure 8. The growth is thought to be due to tungsten hexafluoride migration to the surface, where it reacts to form the growths observed. Magnification of the fibers (fig. 9) shows that they are straight sections joined together to form curved units. They appear to be cylindrical with longitudinal striations. The composition of these fibers, which possess crystalline structure, has eluded X-ray diffraction identification and because of the small amount of material obtained to date, a quantitative analysis was not possible.

CONCLUSION

A method for impregnating polytetrafluoroethylene with the hexafluoride of rhenium, molybdenum, and tungsten was developed. Hydrolyzing the impregnated materials yielded a plastic containing rhenium or molybdenum and, in the case of tungsten impregnation, a fibrous growth on the surface.

It was shown that by soaking polytetrafluoroethylene in rhenium hexafluoride and then hydrolyzing the sample, rhenium oxide was incorporated into the polytetrafluoroethylene sample. The amount of rhenium oxide was shown to be dependent on the length of time the sample was exposed to rhenium hexafluoride. Analysis by X-ray diffraction and electron microscopy showed that the impregnated material contained particles of rhenium oxide. The impregnated polytetrafluoroethylene was also electrically conductive and dependent on the amount of oxide present in the sample. Conductivity 10^{16} times greater than polytetrafluoroethylene ($10^{-18} \text{ ohm}^{-1}\text{-cm}^{-1}$) was observed.

Molybdenum hexafluoride was shown to behave similarly to rhenium hexafluoride, but no conclusive identification of the hydrolysis product was obtained. Indirect evidence

indicated that the hydrolysis product was a mixture of molybdenum oxides. The electrical properties of the material were not investigated.

Tungsten hexafluoride did not behave in the same manner as did the molybdenum and rhenium hexafluorides. During air hydrolysis, a fibrous product of unknown composition was observed to grow on the surface, which is believed to be due to the migration of tungsten hexafluoride to the surface where it was hydrolyzed.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 8, 1968,
120-34-01-09-22.

REFERENCES

1. Leibecki, Harold F.: Screening of Inorganic Compounds as Solvents. NASA TM X-1427, 1967.
2. Ames, I.; and Gregor, L. V.: Preparation and Properties of Thin Films of Molybdenum Oxide. *Electrochem. Tech.*, vol. 2, no. 3-4, Mar.-Apr. 1964, pp. 97-101.

TABLE I. - X-RAY DIFFRACTION

PATTERN OF ReO_2 - Re_2O_3 IN TFE

Intensity ratio, I/I_0	d spacing, \AA (or 10^{-10} m)
6	3.751
4	2.665
2	1.875
5	1.679
1	1.531

TABLE II. - RHENIUM OXIDE PENETRATION AND RESISTANCE

Sample	Weight of oxide, g	Moles TFE per rhenium oxide	Depth of penetration, mm	Specific resistance, ohm-cm			
				ac		dc	
				Method A ^a	Method B ^a	Method A ^a	Method B ^a
Cube 1 ^b	0.0642	31.5	0.8	1.83×10^3	---	31.0×10^3	---
Cube 2 ^c	.1200	22.4	1.2	2.07×10^3	173	5.8×10^3	568

^aMethod B differs from method A by a "back sputtering" cleaning step prior to vapor deposition of the gold.

^bSee fig. 3.

^cSee fig. 4.

TABLE III. - EFFECT OF FREQUENCY
ON CAPACITANCE AND CONDUCTION

Frequency, Hz	Conductivity, $\text{ohm}^{-1}\text{-cm}^{-1}$	Capacitance, F
20×10^3	2.54×10^{-3}	5.0×10^{-3}
15×10^3	2.52	4.9
10×10^3	2.50	5.0
5×10^3	2.49	5.0
1×10^3	2.48	5.1
500	↓	6.0
250		9.2
150		18.3
100		32.9
75		54.0
50		107.3

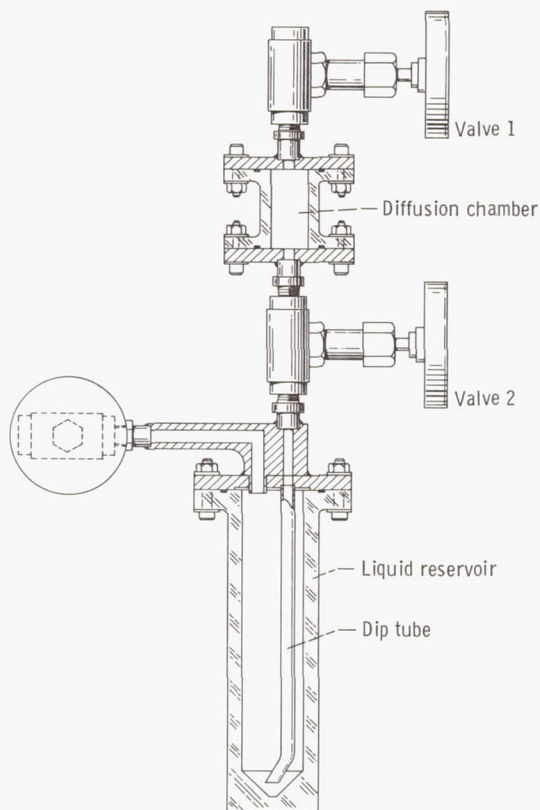
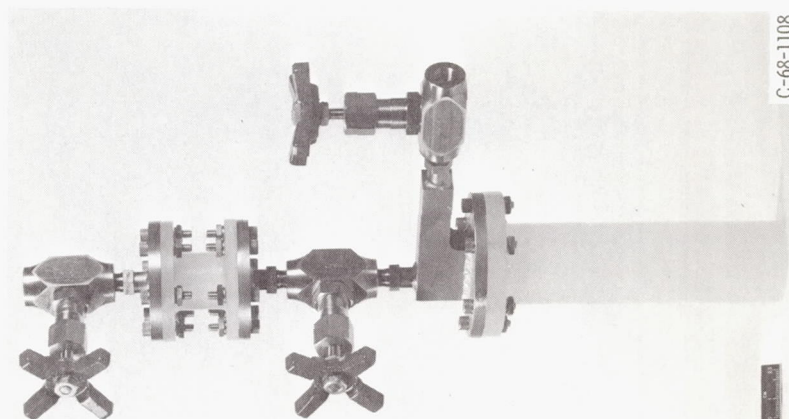
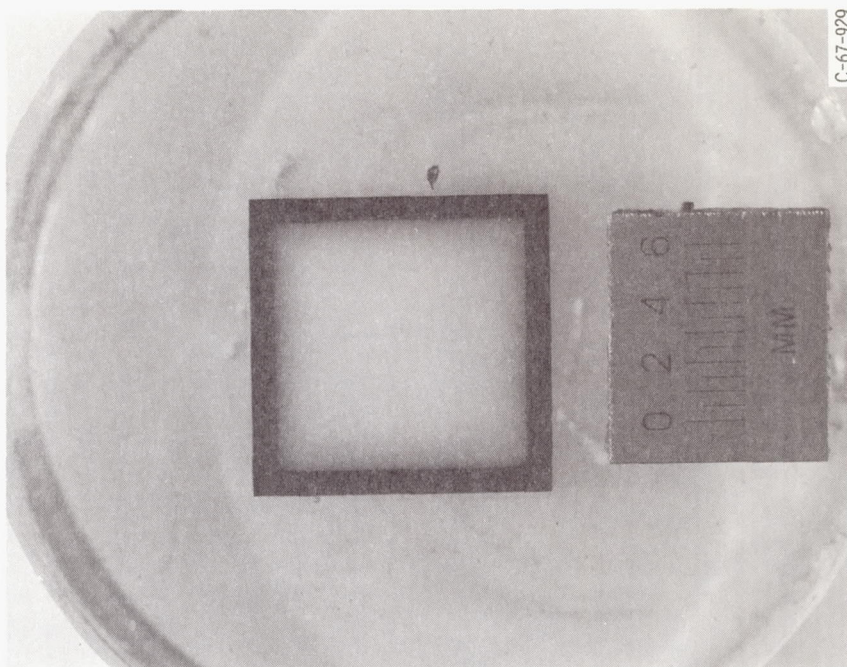


Figure 1. - Schematism of impregnation cell



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Figure 2. - Assembled impregnation cell.



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Figure 3. - Cube 1: polytetrafluoroethylene impregnated with rhenium oxide after 24 hours of rhenium hexafluoride diffusion.

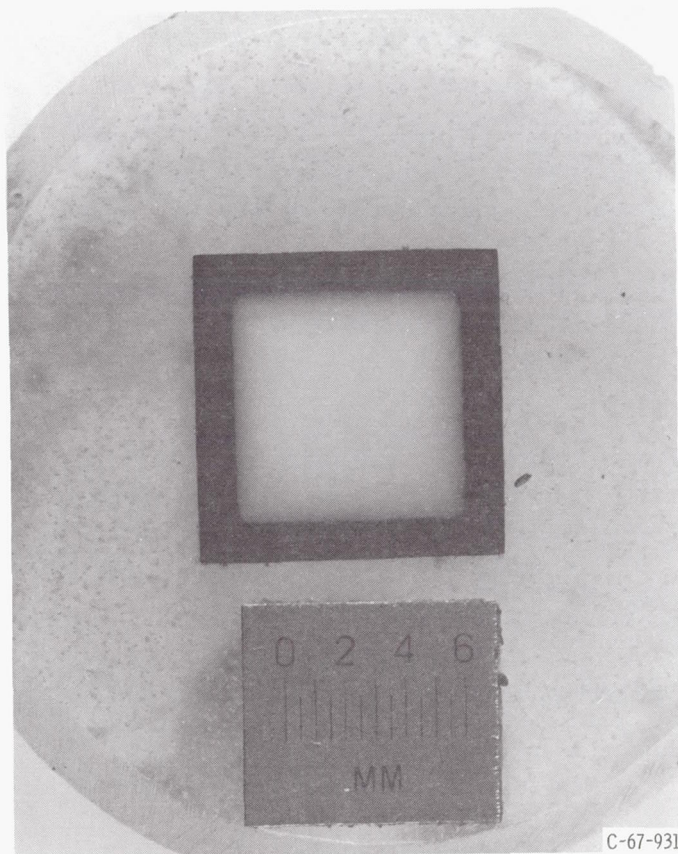
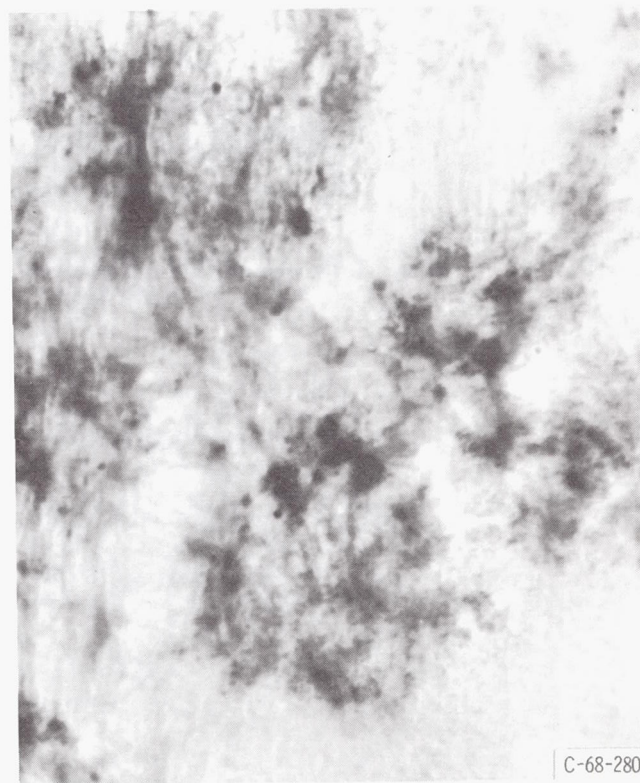


Figure 4. - Cube 2: polytetrafluoroethylene impregnated with rhenium oxide after 72 hours of rhenium hexafluoride diffusion.

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Figure 5. - Electron photomicrographs of rhenium oxide in polytetrafluoroethylene. X15 000.



Figure 6. - Electron photomicrograph of polytetrafluoroethylene showing texture due to blade chatter. X15 000.

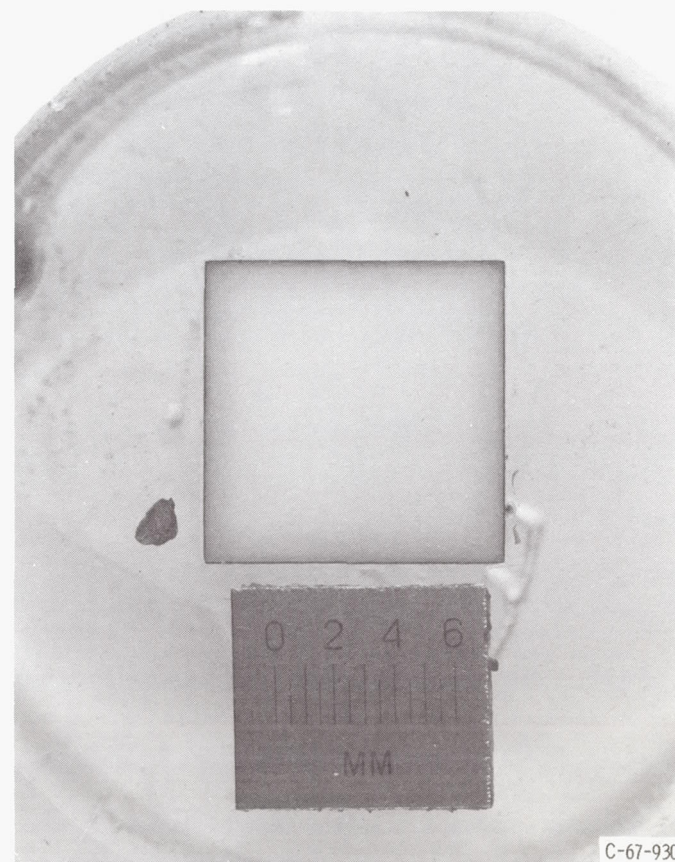
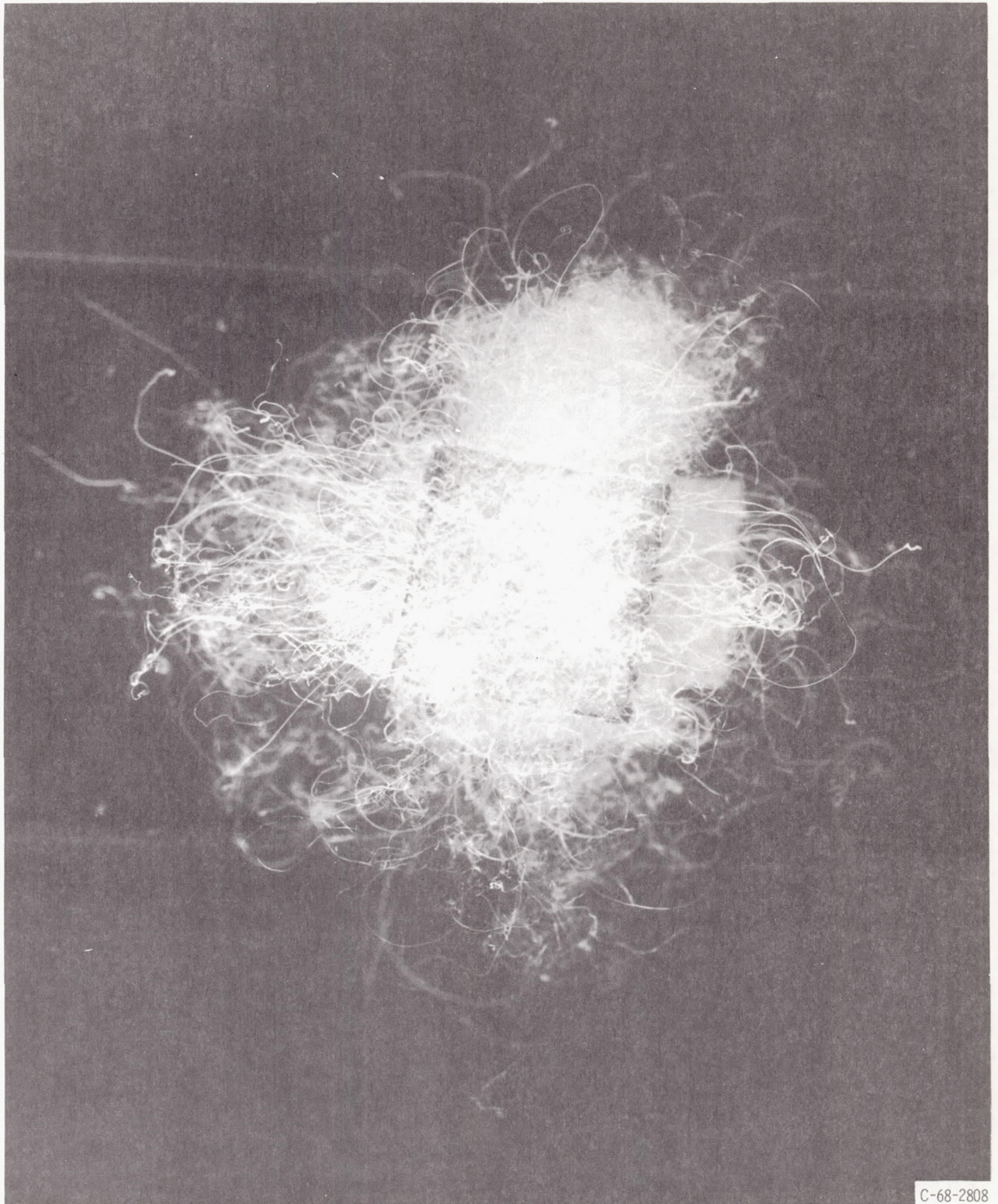


Figure 7. - Polytetrafluoroethylene impregnated with molybdenum oxide.

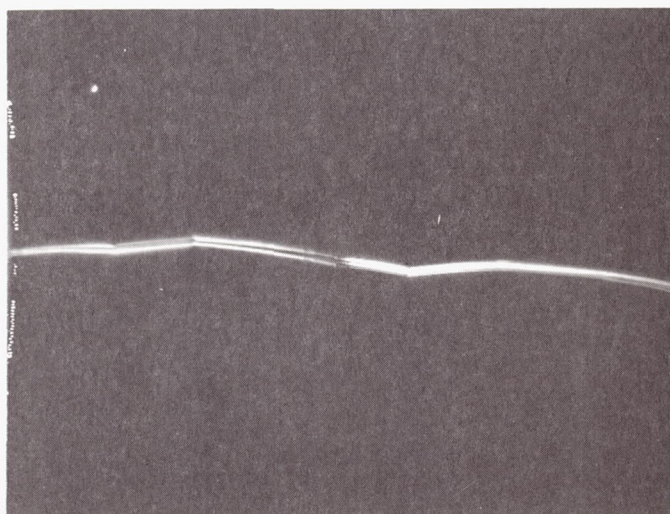


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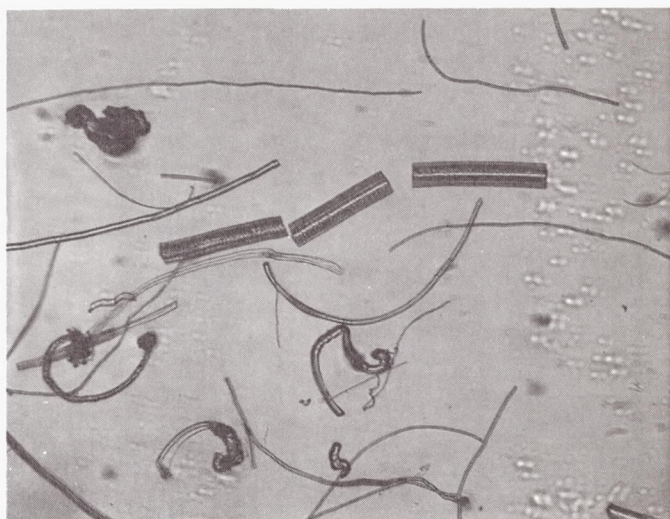
Figure 8. - Polytetrafluorethylene with fibers due to tungsten hexafluoride hydrolysis.



X 500



X 250



X 100

Figure 9. - Fibrous growth from polytetrafluoroethylene.